Renewable fuels and biofuels in a petroleum refinery

Sound judgement of process environment, logistics and product properties is needed to process fossil and bio-derived raw materials on a single site

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Bio-based raw materials and associated process technologies form an entirely new engineering challenge for integrated petroleum refineries. The composition variation of raw materials, including trace components, various logistical problems and the difficulty of coming up with the right integration approach compared to conventional engineering of fuel refineries using petroleum feedstocks, needs new types of skills and experience. The fundamental engineering challenge is to combine existing advanced petroleum process technologies with various aspects of the problems faced in renewable fuels process engineering and to come up with the optimal design approach that enables the implementation of biomaterial streams to the highly integrated process environment of a petroleum refinery.

Introduction
Renewable fuels have been one of the hottest topics so far in this millennium’s energy debate. The reason for the growing interest is obvious: the ever-increasing concern about CO₂ release to the atmosphere and its impact on global warming. Another significant factor is political instability in the areas where crude oil is produced. And thirdly, local agricultural economics and trade deficits, partly due to historically high crude oil prices, provide an additional driver to get more energy from domestic sources among quite a few of the leading consumers of petroleum.

During past centuries, flora has been the source of fuel as well as many valuable and vital substances and constituents. In the oil era, many of those products became cheaper and performed better when derived from fossil feedstocks. For renewable fuels, the sustainable way would be to encourage benefiting first from the value chain of the biomass constituents and to produce fuel only from the residues, or from an entirely different feedstock such as algae — not part of the food chain or the traditional green industry. This method of switching from pollution to solution is already on the research agenda of many enterprises.

The simplest and cheapest way to process renewable feeds in an existing refinery, as co-feeds, is not necessarily the most economical one

Petroleum refinery as a platform for renewable fuels production
Petroleum refineries are natural locations for renewable fuels production. They are, after all, built for the production of advanced fuels by the most cost-effective means to deliver appropriate products for surrounding societies. Refiners are very experienced with their raw materials and equipment, which is mainly due to the fact
that they have been utilising them for a long enough time to gain thorough knowledge on all relevant issues. Typically, the refineries also have an extensive knowledge of product and fuel markets, albeit for petroleum-based fuels only. The processing of biofeedstocks means entering an unknown territory. One could say, from a traditional viewpoint, that anything “bio” means additional problems by way of fouling, decreased efficiencies or an additional work burden. Biomaterials are living organisms containing and producing a multitude of compounds. In traditional applications, the smaller scale impurities might not be relevant or even recognised due to relaxed requirements, but they can be of paramount importance in petroleum refineries with regard to catalyst activity or when accumulating within equipment.

Another important issue is that the simplest and cheapest way to process renewable feeds in an existing refinery, as co-feeds, is not necessarily the most economical one. Also, the available trading specifications for renewable feed materials resemble merely the key factors for present applications, while a complete description of biomaterial properties is lacking. Only experience will reveal the significant factors and surprises.

However, in current circumstances, “bio” also means a premium in product value, which changes the picture, not least in the current economical climate, wherein refinery margins are low or non-existent. The engineering challenge is to do the integration correctly, when bioproducts are manufactured in a petroleum refinery. Moreover, the key is to create molecules as similar as possible to existing fuel molecules in their structures.

Conventional petroleum refineries can be modified to process bio-basestocks into renewable fuels.

**A biorefinery concept could be built on three main initial platforms to promote different product slates**

Figure 1 Biorefinery platforms
product slates (see Figure 1). The sugar platform is based on biochemical conversion processes and focuses on the fermentation of sugars extracted from biomass, including lignocellulosic material. This platform requires strong know-how of bio- and genetic engineering and chemical engineering, because the conversion is done by micro-organisms.

The syngas platform is based on thermochemical conversion processes and focuses on the gasification of variable biomass feedstocks. It can use almost any organic feed and produces synthesis gas that can be converted to components other than fuels. Although the syngas platform seems to consist of known technology blocks that are proven in other applications, there are many challenges that are not simple to overcome. Some of the technology blocks were designed originally for other purposes and applications and, often, quite a few must be redesigned and adapted for this specific application. Also, bio-based feedstocks contain small quantities of components that are different to those of fossil origin, which, of course, requires experimental demonstration.

The constituent platform, based on fractionation processes, focuses on the separation of valuable biomass constituents for further processing. The residues may be utilised by bioconversion or thermochemical means.

**Specific treatment is often necessary for different crude Fischer-Tropsch product streams, which adds to the total engineering burden**

Perhaps the best example of a biorefinery is a traditional pulp mill, a constituent platform, where a primary product, fibres, is separated from chemical constituents using chemical or thermomechanical processes. From the chemical fraction, multiple products may be produced, including commodities, fine chemicals, functional food and pharmaceuticals. Volume-wise, the main by-products so far are different biofuels in liquid or solid form. However, other routes do exist (see Figure 2).

The fats and oils route is currently widely practised in FAME production. It generates a commercial product, which, however, has significantly compromised properties, resulting in blending limitations in normal diesel use or dedicated automotive equipment. The emerging hydroprocessing route provides far superior products and is currently practised in the NExBTL process, with two operating references.
in Neste Oil’s Porvoo refinery and the third unit was started up in Singapore during November 2010. The biomass route depicted in Figure 2 is yet to be fully commercialised.

**Technology challenges**

Proving the credentials of various biorefinery and renewable fuels production concepts in petroleum refineries requires innovation networks and teamwork among different research institutes. One key issue is determining the concept of plant ownership. For a pulp mill or an ethanol plant, the main investor may be self-evident. But the more diverse the mix of expected value-added products, the more complex it is to initiate an organisation or a particular network to promote and finance the project.

The syngas platform requires a reliable logistics chain for raw material feeds where the volumes are huge. For example, a 100 kt/a Fischer-Tropsch (FT) product unit would require more than one million cubic metres of forest residue calculated as solid wood. And the FT product capacity is in most cases too low to be profitable. Today, such logistic chains in high enough volumes are non-existent or at least rare. Partnerships with the forestry industry to secure raw material availability may be more than justified.

Crude FT product is a wide mixture of alkanes, oxygenates and olefins in typically two product streams: condensate and wax. Specific treatment is often necessary for different crude FT product streams, which, of course, adds to the total engineering burden. Co-feed to existing petroleum refinery streams may be one possibility, but it may not be a value-creating solution, because the product of bio-origin is easily diluted in huge amounts of fossil products. In general, a thorough understanding of current oil refining technology and integration skills is
required to achieve a viable solution.

Another challenge is the tremendous variation in raw material qualities. Even for a single tree, the constituent of material changes significantly from base to top or from older branches to buds. Then again, trees from different parts of a single forest or of geographically diverse origins contain different compositions of sulphur, nitrogen and chloride compounds, to name but a few. And things do not ease with farmed raw materials, given the incoherence of the farming industry in general.

Yet another formidable challenge is the management of catalyst cycle length and lifetime, and the required pretreatment know-how and analytics. Clearly, robust processes are required.

**Process development for renewable fuels**

Advanced process modelling is a necessity for the development of processes. This is challenging in view of the lack of property data for natural substances. Therefore, extensive testing of unit operations and unit processes, combined with modelling, gives a reliable base for the process design.

Modelling can be utilised from chemistry to proven technology, by determining the kinetic parameters of reactions, interpreting test results and dimensioning thermal and mass transfer units and emissions management, up to the operational optimisation of the plant. The traditional methodology is illustrated in Figure 3.

However, if advanced modelling technologies and modern chemical engineering tools are used rigorously, significant savings in overall time schedules can be attained (see Figure 4). In practice, the NExBTL process was developed without any conventional pilot plant stage, which cut the time for designing and building such facilities to zero and helped to push technology development forward significantly, enabling the first unit to be started early, resulting in greatly improved NPV for the project. The modelling effort requires time and skills, which, of course, means additional money spent at the front end.

**Partnership is the key**

The ultimate payout with the successful application of modelling can be considerable, as renewable fuel production may be started a year or more before, with no costs associated with piloting. The difference with regard to conventional oil refining and fuel production is that the solutions available might not be tailored to existing needs, but some additional research and engineering is all that is needed to fit the pieces together. A key issue then is to identify suitable partners or resources that are capable of handling this task, since biomaterials have gained a lot of public interest. Many companies would like to participate in the bio-business and are keen to form close relationships and partnerships in the renewables industry. It can be puzzling to have several contestants claiming to be able to handle the task better than...
anyone else, with no grounds to verify this, since it is outside traditional modes of operation. Also, the pros and cons of forming close partnerships must be weighed against whether there truly is potential for mutual benefits (see Figure 5).

An investment project in a petroleum refinery normally means purchasing one or a few licence packages from one or several technology suppliers and finding an engineering contractor who will then put the packages together for the detailed design, construction and purchasing activities. The task is fairly simple, since licence package suppliers are aware of the environment in to which their product is going to be fitted. For renewable fuels processing, a lot is required of the engineering contractor in order to glue together the often misaligned pieces stemming from different industrial practices.

The renewable fuels process can be made to work, but the contractor must step up with a clear vision and fill in the blanks left by technology vendors who could be earning their living in a totally different field of industry, say, with animal feeds.

Generally speaking, for the successful execution of investment in renewables, it is essential to recognise open items in the knowledgebase and to find the right partners to piece the process together. This means managing the whole vendor chain effectively.

**Biomaterials in petroleum refining units**

A wide variety of components is typical for raw materials from natural sources, since living organisms require a multitude of nutrients and minerals for their digestion, which in turn produces a broad spectrum of, say, effluents. Surprisingly, many of the smaller scale impurities and trace components may not even be familiar to the users of present applications if there has not, for one reason or another, been particular interest in them. Often the principle of “if it causes no problem, it is not there” is applied to the variety of impurities. This lack of interest may actually be justified from the producer’s economical viewpoint, but the downside is that the effects of those possibly existing impurities to a different applications cannot be anticipated and they might be revealed only by experience if there has not been previously gained knowledge on their existence and behaviour. Therefore, caution should be applied when studying the specifications for commercially available raw materials — they are by no means complete, and are more likely to incorporate only the properties and parameters that are significant to the present applications of said materials.

**Handling the logistical challenges**

Having said that, renewable raw materials contain a broad spectrum of components in various concentrations, and an experienced refiner might think straight away that it is exactly the same with crude oil, and they would be right. But it must also be noted that even conventional refineries are actually very versatile, with possibly tens of different production units and feed-blending capabilities, while renewable fuels production, especially when integrated into an existing process plant, may consist of a single production unit and a few storage tanks. If so, there should be no false expectations of the unit being capable of processing “any” of the types of raw material chosen to be utilised.

When the basis of design is agreed for a new renewable fuels process, the natural variation in raw material quality can be addressed in two ways. The
first is, obviously, to specify all of the possible variations of raw materials as suitable feeds for the process, but this can end up raising the complexity of engineering, which unfortunately applies to costs as well. Another approach would then be to limit the number of raw materials to a few representative cases and compensate for variations by designing the logistics as flexible as possible. In practice, this would mean providing enough storage capacity and routing possibilities in order to keep some fractions separate, to blend fractions intentionally and for the intermediate storage of fractions that require severe processing.

**Purification of oils and fats**

Since the purification of oils and fats is a common task in the food industry, there are several well-developed processing methods commercially available, including degumming, bleaching, deodorising and dewaxing. Some can be alternatives to one another, while others are connected in series to achieve best results.

The choice of suitable purification method depends very much on the quality and source of the oil to be purified. Some seed oils may need additional steps to reach the required levels of purity. But it is also good to recognise that the processing conditions within one purification step can vary with different feedstocks.

When designing a new processing unit for renewable fuels production, it can be tempting to make the range of possible feedstocks as wide as possible. By considering what was stated above, it becomes obvious that the purification system, whatever the combination of steps chosen, must be flexible in terms of utilising the processing steps. If some feedstocks require less purification, maybe one step can be completely bypassed. The possibility then is not only for an actual bypass pipeline over one processing step, but also the ability to store feedstocks with different requirements separately.

The size and frequency of certain feedstock shipments must be taken into account when designing the storage facilities if blending is not desired. On the other hand, having some blending and buffering capacity in between processing steps might be advantageous, because it allows intermittent operation of one processing step while securing homogenous feed quality for the next.

Flexibility can be greatly increased with logistical solutions. Processing units in general tend to be designed for a certain capacity, which then can vary to some extent between given turndown and over-design percentages. With properly designed logistics, the virtual turndown or operating window of processing steps can be significantly improved.

**Managing by-product and waste streams**

Integrating the renewable fuels process into an existing refinery can result in the co-processing of raw materials from fossil and renewable sources. But it may also turn out to be beneficial to keep these two fractions separated for legislative and/or economical reasons; for instance, in the search for a premium margin.

In principle, separation is very simple; it is all about nominated storage tanks, pipelines and processing units. The real challenge of integration, however, is how to manage all of the side products, waste streams, drains and spills without introducing a threat to the existing plant operations (see Figure 6). A good example is handling wastewater from a process using renewable raw materials. Due to their composition and biological source, the trace amounts of raw materials in water effluents can create order of magnitude greater BOD readings compared to common oily waters. In addition, the biological compounds are often more easily digested by the fauna in active sludge treatment and, therefore, the species in sludge used to digest biological wastewater are often different from those used for fossil organic waters. It can be easily understood that there is a good potential to mess up or overload the wastewater facility without proper knowledge. A seemingly small issue may become a very large one when the whole facility has to be run down because of malfunctioning wastewater treatment. A similar issue could be the transportation of renewable raw material trace components to another fossil unit via, for instance, a minor utility line, which could appear after a time as mysterious corrosion or plugging.

**Product compatibility**

All products coming from a petroleum refinery pipeline
must comply with existing specifications and simultaneously ensure future product improvement. However, this is not the case depicted in Table 1, which shows some key gasoline components and their key quality parameters.

As can be seen, compared to common fuel components, the existing biocomponents perform quite well, although only ETBE and TAEE bring considerable advantages in upgrading gasoline blending. The situation with diesel material is even worse, as fatty acid methyl esters have provided many problems due to poor product stability, cold properties and challenges in engine performance (deposits and corrosion in fuel systems, engine oil dilution or polymerisation, phosphorous, ash). These problems can be overcome by hydrogenated vegetable oils and animal fats, such as the product from Neste Oil’s NExBTL process, which simultaneously yields superior product with improved cetane and lower emissions. The key is to create molecules, be they in gasoline or diesel boiling range, which are as similar as possible to existing fuel materials in their structure.

Conclusions
Both biorefining and renewable fuels production in petroleum refineries pose many challenges. As both are strongly emerging ways to produce fuels, the underlying engineering skills requirements combined with sound judgement of process environment, logistics and respective product properties and values will dictate the overall feasibility of such operations.

The engineering challenge is to combine existing advanced petroleum process technologies with various aspects of the problems faced in biorefinery engineering and to come up with process simulation tools that allow the implementation of biomaterial streams to the highly integrated process environment of a petroleum refinery. Besides process modelling, a sound understanding of related material requirements and corrosion engineering, as well as advanced process control and on-line analyser technologies permit the steady-state operation levels required in a modern petroleum refinery. The resulting most viable solution is the one entailing the best economic results.

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**Figure 6** Production segregation

**Table 1**

<table>
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<th>Butanes</th>
<th>High octane</th>
<th>Low RVP</th>
<th>Low olefins</th>
<th>Low benzene</th>
<th>Low aromatics</th>
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